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PHOTOREACTIONS OF AZIDOFORMATES WITH ETHYL AZIDOFORMATE AND WITH DIETHYL AZODIFORMATE

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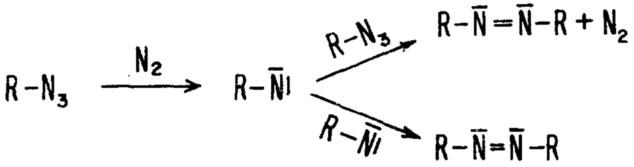
The decomposition of azides to give azo compounds has been reported for carbamoyl- and aryl-azides.[1,2,3,4] The reaction can be formulated as proceeding by the attack of a nitrene intermediate on azide, or even as the dimerization of the nitrene:

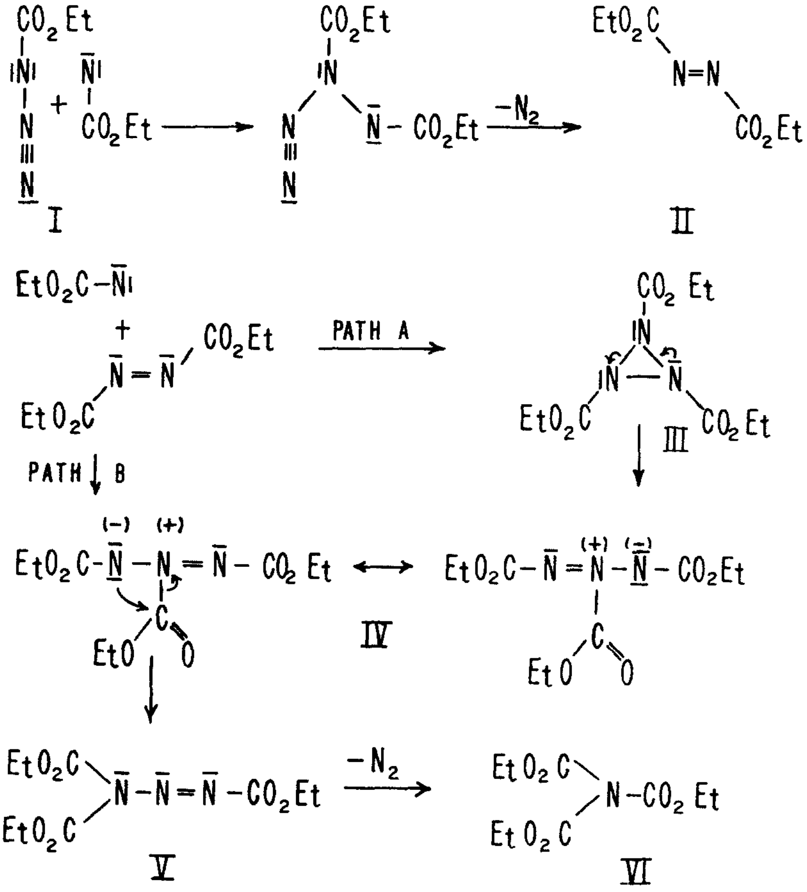


Such reactions have, therefore, been taken as evidence for the formation of a nitrene intermediate.[3,4]

We have found that diethyl azodiformate is formed in the flash photolysis of gaseous ethyl azidoformate[5] and in the photolysis and thermolysis of neat, liquid ethyl azidoformate. The liquid state reaction was monitored by subjecting aliquots to vapor phase chromatographic analysis. At first, a concentration of diethyl azodiformate (II) is seen to build up. When it reaches about 5%, triethyl nitrilotriformate (VI) becomes apparent. The concentration of the azo compound II rises to about 30%, then decreases and becomes zero at the end of the reaction. The concentration of VI increases correspondingly. A total yield of 58% of VI is formed, along with a 94% yield of nitrogen (calculated on the basis of the formation of VI --

$4N_2$ from 3 molecules of azide). II was identified by v.p.c. retention time and comparison of its infrared spectrum with that of an authentic sample. VI was identified by elemental analysis, n.m.r. spectrum, and by comparison of its infrared spectrum with that of an authentic sample.

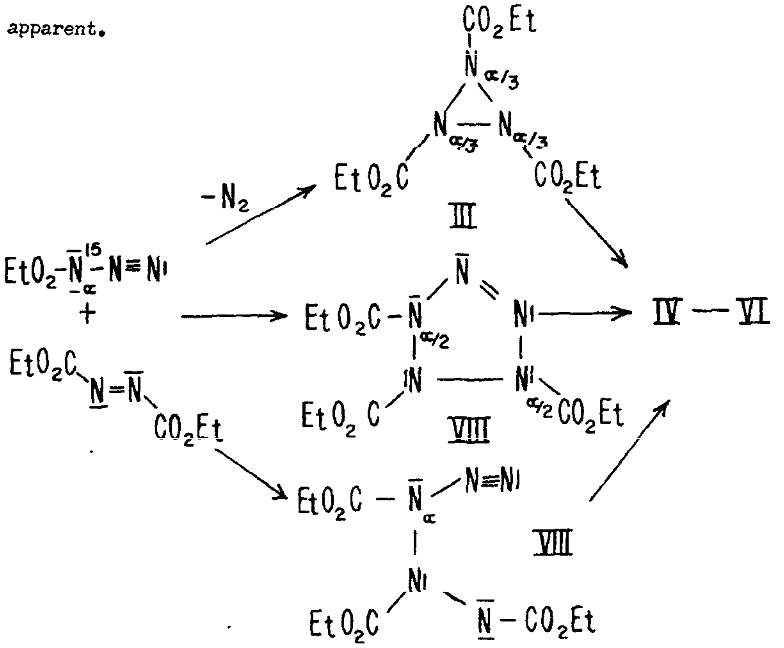
One might be tempted to write a nitrene mechanism:



That the nitrilotriformate (VI) is indeed a product from the azide (I) and the azo compound (II) is proven by photolysis of a mixture of methyl azidoformate and diethyl azodiformate. Monomethyl diethyl nitrilotriformate is formed in 25% yield.

Carbethoxynitrene can be generated not only by decomposition of ethyl azidoformate[6] but also by α-elimination from p-nitrobenzenesulfonoxy urethane.[7] The α-elimination produces the same products or product mixtures as does the photodecomposition of ethylazidoformate when run in benzene,[7] (ring expansion of the aromatic ring), cyclohexene[7,8] (addition to the double bond and three C-H- insertion products), cyclohexane[7] (C-H-insertion), or acetonitrile[9] (cycloaddition to an oxadiazole). The near identity of even the product ratios in these reactions indicates that both sources produce the same nitrene. When carbethoxynitrene is generated by α-elimination in ethyl azidoformate, no diethyl azodiformate can be found by v.p.c. analysis. When cyclohexane is added to the reaction mixture, cyclohexylurethane is produced, demonstrating the presence of the nitrene. Generating, by α-elimination, carbethoxynitrene in the presence of one equivalent of diethyl azodiformate leads to the recovery of 75% of the unchanged azo compound. Employing a tenfold excess of the nitrene consumes almost all of the azo compound (II), but no triethyl nitrilotriformate is produced in either case. The product mixture formed does not contain the same components as does the product mixture from the azide I and carbethoxynitrene, as shown by v.p.c. analysis. Thus, it appears that the reaction of carbethoxynitrene with ethyl azidoformate does not produce the azo compound II, and that reaction of the latter with carbethoxynitrene does not produce nitrilotriformate VI. We conclude that an excited molecule of the azide I reacts with another molecule of I before it decomposes to carbethoxynitrene and nitrogen.

At present, we have no information on the transition state or intermediate that leads, with loss of nitrogen, to II. The reaction of diethyl azodiformate (II) with the azide I presumably involves attack of excited azo compound on azide. Attack of excited azide seems less probable, in view of the ready decomposition of excited I to carbethoxynitrene and nitrogen which would compete with an intermolecular reaction with II, present in low concentration when the formation of VI becomes apparent.



The intermediacy of a triazacyclopropane III might be demonstrated by using N^{15}_{α} labeled azide and would result in VI containing 1/3 of the label. A path through VII or VIII would give VI with 1/2 of the label.

It appears that the formation of azo compounds from azides cannot be used as evidence for the formation of nitrene intermediates. We are studying further the reactions of azides with azides and with azo compounds.

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